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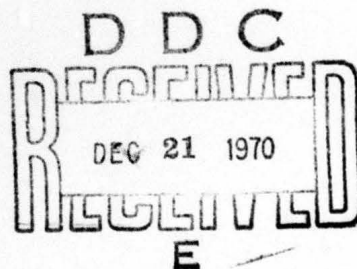
TECHNICAL REPORT NO. 29

**DIFFERENTIAL CAPACITANCE STUDY OF STRESS-ANNEALED
PYROLYTIC GRAPHITE ELECTRODES**

by

Jean-Paul Randin and Ernest Yeager

1 November 1970



**Office of Naval Research
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13. ABSTRACT

The non-faradaic capacity of electrodes prepared from high pressure stress-annealed pyrolytic graphite has been examined in aqueous solutions using an a.c. impedance bridge. Such materials have a rocking angle (x-ray diffraction) as small as 0.4° and the properties of surfaces oriented parallel to the basal plane approach rather closely those of single crystal graphite. The differential capacity measured on this surface has a near parabolic dependence on electrode potential with no evidence of a hump and a minimum of $\sim 3 \mu\text{f}/\text{cm}^2$ in 0.9 M NaF . This low value is explained on the basis that a substantial fraction of the potential change between the electrode bulk and the solution bulk occurs across a space charge layer within the graphite.

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Differential Capacitance Study of Stress-Annealed
Pyrolytic Graphite Electrodes

by

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ABSTRACT

The non-faradaic capacity of electrodes prepared from high pressure stress-annealed pyrolytic graphite has been examined in aqueous solutions using an a.c. impedance bridge. Such materials have a rocking angle (x-ray diffraction) as small as 0.4° and the properties of surfaces oriented parallel to the basal plane approach rather closely those of single crystal graphite. The differential capacity measured on this surface has a near parabolic dependence on electrode potential with no evidence of a hump and a minimum of $\sim 3\mu\text{f}/\text{cm}^2$ in 0.9 M NaF . This low value is explained on the basis that a substantial fraction of the potential change between the electrode bulk and the solution bulk occurs across a space charge layer within the graphite.

In recent years, high pressure stress-annealed pyrolytic graphite has become available. This material has a near perfect orientation along the c-axis and its structure is much more defined than that of the pyrolytic graphite used by prior workers (1). The basal plane of this material provides a rare opportunity to study the electrochemical properties of a surface in which all the surface valencies are satisfied in the plane of the surface.

The present study has been directed to the study of the differential capacity of this surface in aqueous solutions using an a.c. impedance bridge.

Experimental

The stress-annealed pyrolytic graphite used in this study^a showed a rocking curve whose mosaic spread is approximately 0.3 to 0.4° width at half-maximum intensity of the (002) x-ray diffraction line. The measured 2d interplanar spacing is $6.713 \pm 0.002 \text{ \AA}$ compared to $6.7078 \pm 0.0002 \text{ \AA}$ for the single crystal. The graphite electrodes were machined under compression into circular disks with a diameter of 5 mm. These graphite disks, backed with nickel to increase their mechanical strength, were then press-fitted into a Teflon holder. A fresh electrode surface was exposed for each experiment by placing a piece of plastic adhesive tape, cut to the exact size, in contact with the graphite surface and then peeling off a layer of graphite with the tape. Care was taken not

^a Supplied by the Union Carbide Technical Center Research, Parma, Ohio, 44130.

to contaminate the Teflon surrounding the graphite disk with the adhesive on the plastic tape. The graphite surface so exposed had the appearance of a black mirror and no plane other than the basal plane has been observed by microscopic examination under 800X magnification.

The electrochemical cell was made entirely of Teflon. The main compartment contained the working electrode and a 99.99% gold disk shaped counter electrode (9 cm diameter, 0.01 cm thick) located parallel to the working electrode at a distance of about 4 cm with one side against the bottom of the Teflon cell. This electrode was used for only the a.c. impedance measurements. Gold was chosen for the counter electrode since it should not dissolve in helium-saturated sodium fluoride solutions. Two separate compartments were connected to the central compartment for the auxiliary and reference electrodes. The auxiliary electrode was used for the d.c. polarization of the working electrode. Both the auxiliary and reference electrodes were 99.99% palladium foil (2.9 cm diameter, 0.01 cm thick) over the rear of which was passed purified hydrogen. The reference electrode compartment was connected to the main compartment via a Luggin capillary, while the auxiliary compartment was connected to the main compartment by a short tube (1 cm diameter, 5 cm long), filled with the same solution as the main compartment. The auxiliary and reference Pd electrodes were charged with hydrogen (purified with an Englehard Industries Pd-Ag alloy diffuser) in order to form a stable H-Pd alloy, the β -phase (2).

The experiments were performed in a nitrogen atmosphere glove box to reduce contamination by atmospheric components and to minimize possible incorporation of dust and dirt in the cell. Nitrogen was con-

tinuously purged through the box.

The solutions of sodium fluoride (Baker Analyzed Reagent) were prepared by dissolution in nitrogen-saturated triple distilled water (second distillation from alkaline permanganate). Trace contaminants were removed by treatment of the electrolyte with purified active charcoal and in situ pre-electrolysis performed with a 50 cm² gold cathode in the main compartment polarized to -0.9 V vs the H/ β -Pd reference for at least 24 hr with helium bubbling. The helium was purified with copper turnings maintained at about 450°C and molecular sieves (Linde type 3A and 13X). This gas was bubbled through the solution before and during the measurements.

The measurements of the equivalent series capacitances and resistances were carried out at 25°C with an a.c. bridge and polarization circuit. This bridge has been checked with standard resistance and capacitance components and found to contribute a negligible error over the range of frequencies covered in this paper (100Hz to 20 KHz). The a.c. voltage applied to the cell did not exceed a few millivolts.

All capacitances are given in terms of apparent electrode area. The true area has not been taken into account but the ratio of the true to apparent area should be essentially unity for the basal plane of stress-annealed pyrolytic graphite.

Results and Discussion

In a recent paper, Bauer, Spritzer and Elving (1) studied the differential capacity of a pyrolytic graphite disk electrode whose structural

characteristics were not defined in the paper. These authors observed a frequency dependence of both the series capacitance and resistance. Bauer et al. suggested that this frequency dispersion might be at least in part the result of the electrode geometry since the distribution of current at a disk electrode is not uniform across the surface.

Preliminary measurements in the present study also showed a frequency dispersion. Consequently, an attempt was made to minimize the non-uniform current distribution on the disk solid electrode surface by using a Teflon hood of the type shown in Fig. 1. A circular lip which made a line seal with the graphite electrode was incorporated in the Teflon hood. The internal diameter of the hood (4 mm) was smaller than that of the graphite disk (5 mm). The depth of the hood was chosen to be the same as its diameter, i.e., 4 mm. Preliminary tests showed that this dimension had no significant effect on the frequency dispersion.

Beside providing a more uniform current distribution on the electrode, the hood restricted the effective area of the electrode to the center of the disk and hence minimized problems associated with orientations other than the basal plane, present along the periphery of the disk where it fitted into the Teflon holder. Measurements on the edge orientation (plane perpendicular to the basal plane) indicate capacities of at least one order of magnitude higher than on the basal plane and hence even a small fraction of the surface other than the basal orientation can lead to a serious error.

The frequency dispersion for the basal plane of stress-annealed pyrolytic graphite in 0.9 M NaF is shown on Fig. 2. Without the hood,

the magnitude of the dispersion is comparable with that reported by Bauer et al. (1), although not as large. With the Teflon hood the frequency dispersion is negligible (see Fig. 2), provided the hood is slipped on to a freshly peeled dry electrode. On the other hand a small frequency dispersion is evident (see Fig. 2) if the hood is slipped on to a wet electrode, prepared by peeling off a layer from the basal plane under the surface of electrolyte in a separate container and then transferred wet within the N_2 -filled glove box into the cell. This frequency dispersion is attributed to the electrolyte film between the graphite surface and the Teflon hood. When the two surfaces are dry, the small gap between the hood and the portion of the graphite covered by it does not normally fill with electrolyte because of the hydrophobic properties of the two surfaces.

Usually the capacity measured on the electrode peeled off dry was lower than that of the same electrode peeled off under the electrolyte. The reproducibility of the capacity at a given frequency also was less with electrodes peeled in either air or the nitrogen within the glove box rather than under the surface of the electrolyte. Under extreme conditions, the variation in capacity was as much as 100% with the electrodes peeled dry as compared with a variation of only 5% for electrodes peeled wet. Consequently all further measurements reported in this paper have been carried out with electrodes peeled off under electrolyte and the hood subsequently slipped on.

The lack of any appreciable frequency dispersion in 0.9 M NaF on the basal plane of stress-annealed pyrolytic graphite with the Teflon

hood is to be expected for a solid electrode provided the surface roughness is small. The mirror-like appearance of the surface with direct visual examination as well as microscope examination (800X) both imply that surface roughness is very small. In the case of a semiconductor electrode (see the following discussion), the lack of frequency dispersion at audio frequencies also implies either that the surface electronic states contribute very little to the observed capacity on the basal plane or that the surface electronic states have very short or very long relaxation times.

The capacity measured at a fixed potential on the basal plane also decreased slowly with time. This decrease was usually smaller than 3% in 15 min with electrodes peeled wet while the series resistance remained virtually constant. This rate of decrease did not vary significantly with the applied potential in the range +0.5 to -0.5V re NHE, with the frequency in the range 100Hz to 20KHz, or with stirring. The rate of decrease was smaller with electrodes peeled off under electrolyte than peeled dry.

Since the time dependence of the capacity on the basal plane of wet peeled electrodes was so small, the capacity-potential curves measured point by point were essentially the same regardless of whether the values were measured with increasingly anodic or cathodic potentials. The values indicated in Fig. 3 were recorded point by point with potential increasing in the anodic direction. The shape of the capacity-potential curve is nearly symmetrical with respect to the minimum, is independent of the concentration of the electrolyte at concentrations

in the range 0.01 to 1.0 M, and does not exhibit the hump usually observed on metallic electrodes. The shape of the capacity-potential curve does not depend significantly on the way the electrode surface has been renewed (peeled wet or dry).

The value of the apparent capacity at the minimum of the capacity-potential curve is low, i.e., $\sim 3 \mu\text{f}/\text{cm}^2$, compared with values usually higher than $15 \mu\text{f}/\text{cm}^2$ for metallic electrodes. In contrast, the apparent capacity at the minimum of the capacity-potential curve is about $16 \mu\text{f}/\text{cm}^2$ for the polished basal plane of ordinary pyrolytic graphite ($\Delta\theta_{1/2} \simeq 40^\circ$). Furthermore, the minimum capacity is 50 to $70 \mu\text{f}/\text{cm}^2$ for the polished edge orientation of stress-annealed pyrolytic graphite ($\Delta\theta_{1/2} \simeq 0.4^\circ$).

Table I compares the capacity data for ordinary and stress-annealed pyrolytic graphite obtained by Bauer et al. (1) and in the present study. Bauer et al. (1) reported values ranging from $\sim 12 \mu\text{f}/\text{cm}^2$ for the surface prepared by cleaving to $\sim 60 \mu\text{f}/\text{cm}^2$ for the polished basal plane of ordinary pyrolytic graphite measured at 1000 Hz. The insert in Fig. 3 gives the capacity-potential curve based on the data reported by these authors. The minimum value of the capacity as well as the potential dependence reported by these authors deviate substantially from that found on the basal plane of stress-annealed pyrolytic graphite in the present study. The minimum value of the capacity reported by Bauer et al. for the polished basal plane of ordinary pyrolytic graphite, i.e., $\sim 60 \mu\text{f}/\text{cm}^2$, should be compared with $\sim 16 \mu\text{f}/\text{cm}^2$ found in the present study for the same orientation of polished ordinary pyrolytic graphite. The different origin and preparation of the sample are probably responsible for the

discrepancy.

Table I. Comparison of capacity data for ordinary and stress-annealed pyrolytic graphite.

	Bauer <u>et al.</u> (1)	present work
ordinary pyrolytic graphite		
basal plane, cleaved	12 $\mu\text{f}/\text{cm}^2$	
basal plane, polished	60	16 $\mu\text{f}/\text{cm}^2$
stress-annealed pyrolytic graphite		
basal plane, peeled off	-	3
edge orientation, polished	-	50 - 70

The capacity measured on the basal plane of the graphite specimens with very small rocking angles (e.g., $\Delta\theta_{1/2} \simeq 0.4^\circ$) should approach the value for this plane on single crystal graphite. The minimum capacity of $\sim 3\mu\text{f}/\text{cm}^2$ observed on the basal plane of such stress-annealed pyrolytic graphite is far too low to be explained on the basis of the usual ionic double layer structure within the electrolyte.

The differential capacitance of a semiconductor or semi-metallic electrode-electrolyte interface is composed of three series components: the capacitance of the space charge layer within the semiconductor, that of the compact double layer, and that of the diffuse ionic layer of the electrolyte. For electrolytes of high concentrations, e.g., 1M,

the capacitance of the diffuse ionic layer is usually large, i.e., $> 100 \mu\text{f}/\text{cm}^2$, compared to the other two components. In this case, its contribution to the total capacitance is therefore negligible. The capacitance associated with the compact layer is expected to have a value of 10 to $20 \mu\text{f}/\text{cm}^2$ in the absence of surface states on the basis of the values encountered with metal electrodes. The capacity of the compact double layer on the basal plane of graphite may differ appreciably from this value due to the non-polar nature of the graphite surface but it seems quite unlikely that this difference would amount to almost an order of magnitude. Consequently, the low observed capacity is best attributed to the space charge component within the graphite.

Unfortunately, the electrical properties (resistivity, carrier concentrations, and mobilities) are not known specifically for the materials used in the present study. For similar stress-annealed pyrolytic graphite, Spain, et al. (3) have reported a resistivity in the basal plane of $\sim 40 \mu\text{ohm}/\text{cm}$ and a charge carrier mobility of $1.2 \cdot 10^4 \text{ cm}^2/\text{V-sec}$ at room temperature. In contrast, along the c-axis the resistivity of the same material is 0.15 ohm-cm according to the same authors. For heat treated pyrolytic graphite without stress-annealing, the charge carrier mobility along the c-axis has been reported (4) to be $\sim 3 \text{ cm}^2/\text{V-sec}$ at room temperature. Also at room temperature, the following total carrier concentrations have been reported: for naturally occurring graphite single crystals, $9.9 \text{ to } 10.1 \cdot 10^{18} \text{ carriers}/\text{cm}^3$ (5); for heat treated pyrolytic graphite, $1.2 \cdot 10^{19}$ (4), $1.1 \cdot 10^{19}$ (6) and

$1.4 \cdot 10^{19}$ carriers/cm³ (7). The ratio of the mobility of the electrons to that of the holes ($b = \mu_e/\mu_h$) was found to be 1.1 at room temperature (3,5,6) for both heat treated and stress-annealed pyrolytic graphite.

The theory of semiconductor electrodes indicates that the capacitance of the space charge layer in a pure intrinsic semiconductor should exhibit a minimum value given by the expression^b (8)

$$C_o = \left[\frac{\epsilon \epsilon_o e^2 c}{2\pi kT} \right]^{1/2} \quad (1)$$

with the dependence of the capacity on potential given as:

$$C_{sc} = C_o \cosh\left(\frac{\phi e}{2kT}\right) \quad (2)$$

where ϵ = dielectric constant

ϵ_o = permittivity

e = absolute value of electronic charge

c = electronic charge carrier density

k = Boltzmann's constant

T = absolute temperature

ϕ = potential at the surface

The only values apparently available for the dielectric constant are

^b Bohnenkamp and Engell (8) have omitted a factor of 4π in the expression giving the charge distribution in terms of the Poisson equation. This has been corrected in the formula given above.

those from optical measurements rather than at audio frequencies.

According to Ergun et al. (9) the value of ϵ at 5461 Å in the basal plane is 2.61 and along the c-axis is 3.28.

Using the value of 6.10^{18} carriers/cm³ for the electronic carrier concentration and 3 for the dielectric constant, C_0 is 1.3 $\mu\text{f}/\text{cm}^2$ as compared to $\sim 3 \mu\text{f}/\text{cm}^2$ for the experimental value.

The comparison of the calculated C_0 value with the experimental value is reasonable, considering the uncertainty as to c and ϵ . The potential dependence of the space charge capacity represented by eq. (2), however, is much greater than that observed experimentally in Fig. 3. Possible factors responsible for this discrepancy are

a. imperfections on the exposed basal plane, giving use to sites other than those with completely satisfied valencies and resulting in degenerate surface electronic states. In the case of germanium electrodes, Gerischer (10) has given a theoretical treatment which shows that the space charge capacity depends relatively little on polarization in the potential region of surface degeneracy.

b. The applicability of the presently available semiconductor theory to a system such as graphite with a total carrier concentration as high as 10^{19} carriers/cm³ and hence with Debye lengths comparable to the lattice dimensions is open to serious question.

In order to explore further the importance of the semiconductor properties of graphite in controlling the observed differential capacitance, measurements are being undertaken with boronated stress-annealed pyrolytic graphite which exhibits p-type semiconducting char-

acteristics. Studies involving the effect of anions which normally specifically adsorb on ordinary electrodes, for example, iodide, are also in progress and will be reported later.

The data included in this paper show that the differential capacitance of the basal plane of stress-annealed pyrolytic graphite-electrolyte interface is quite abnormal and that the space charge characteristics of graphite must be taken into account in examining the electrochemical properties of this material.

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REFERENCES

1. H. H. Bauer, M. S. Spritzer and P. J. Elving, J. Electroanal. Chem., 17, 299 (1968).
2. D. J. G. Ives and G. I. Janz, "Reference Electrodes", Academic Press, New York (1961) p. 112-116.
3. I. L. Spain, A. R. Ubbelohde, and D. A. Young, Phil. Trans. Roy. Soc. London, Ser. A, 262 (1128), 345 (1967).
4. C. A. Klein, J. Appl. Phys. 33, 3338 (1962).
5. D. E. Soule, Phys. Rev., 112, 698 (1958).
6. C. A. Klein and W. D. Straub, Phys. Rev. 123, 1581 (1961).
7. C. A. Klein, Rev. Mod. Phys., 34, 72 (1962).
8. K. Bohnenkamp and H. J. Engell, Z. Elektrochem., 61, 1184 ;(1957).
9. S. Ergun, J. B. Yasinsky and J. R. Townsend, Carbon, 5, 403 (1967).
10. H. Gerischer, "Semiconductor Electrode Reactions", in "Advances in Electrochemistry and Electrochemical Engineering", (P. Delahay, ed.) Vol. 1, Interscience Publishers, New York (1961) p. 139.

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□ without hood, layer peeled off under electrolyte,
○ with hood, layer peeled off dry,
● with hood, layer peeled off under electrolyte.
- Fig. 3 Capacity-potential curves for the basal plane of stress-annealed pyrolytic graphite in NaF (pH \sim 6) at 25°C and 1000 Hz. With hood, layer peeled off under electrolyte.
● 0.9 M NaF
○ 0.1 M NaF
Insert figure: Bauer, Spritzer and Elving (1) data in 0.5 M KCl; resurfaced by polishing; frequency: 1000 Hz.

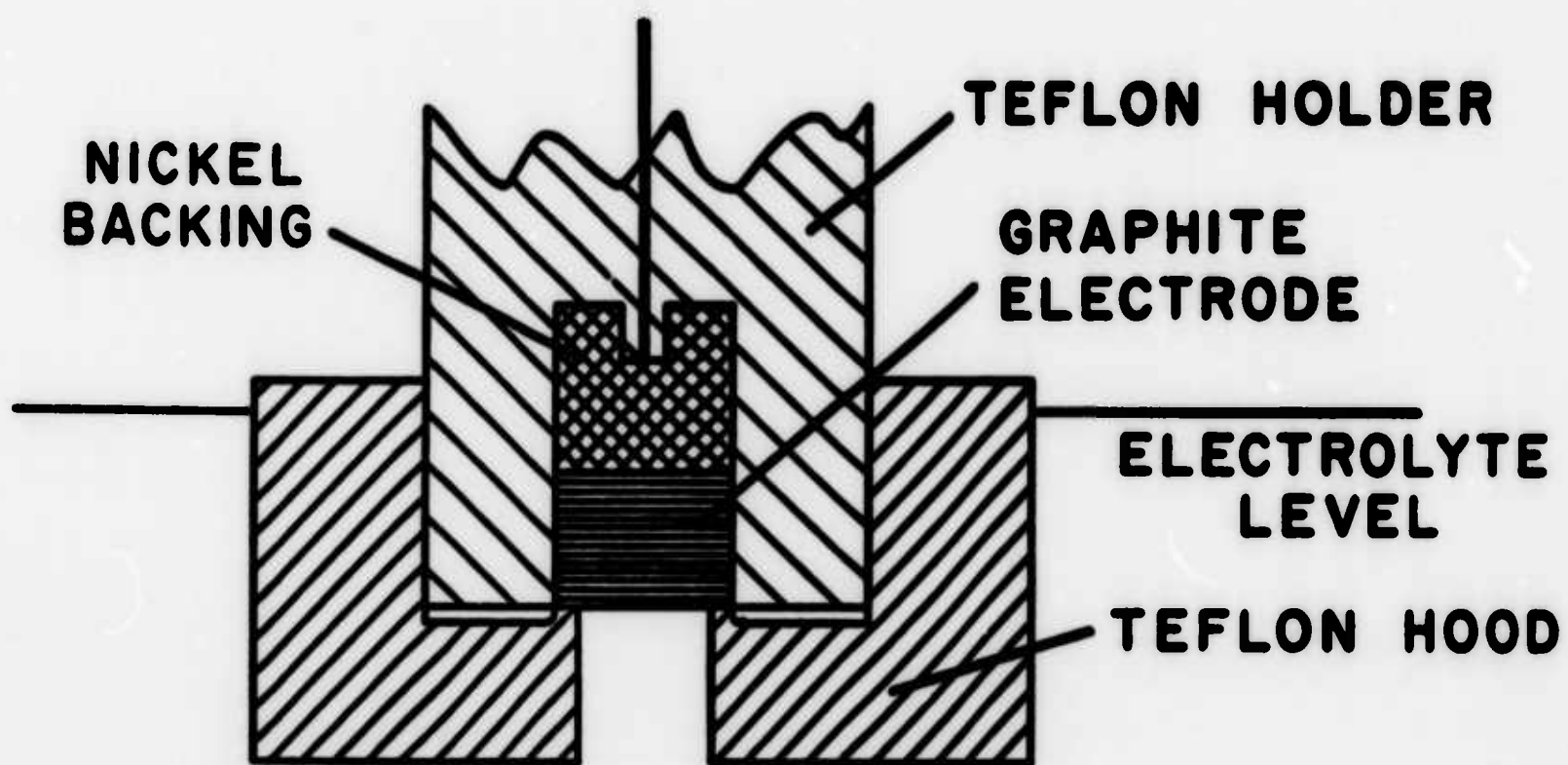


Fig. 1 Cross section of the graphite electrode holder and hood.

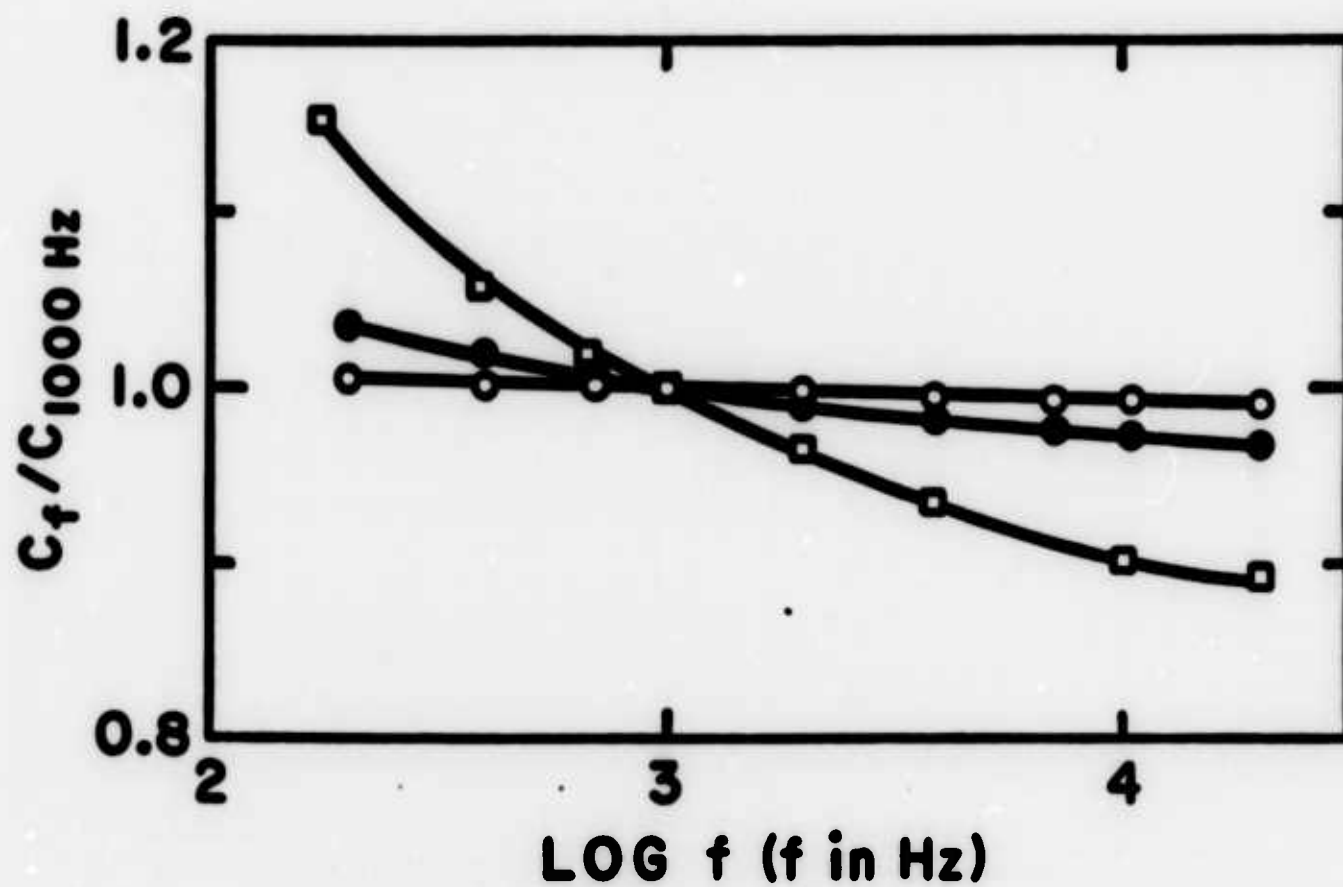


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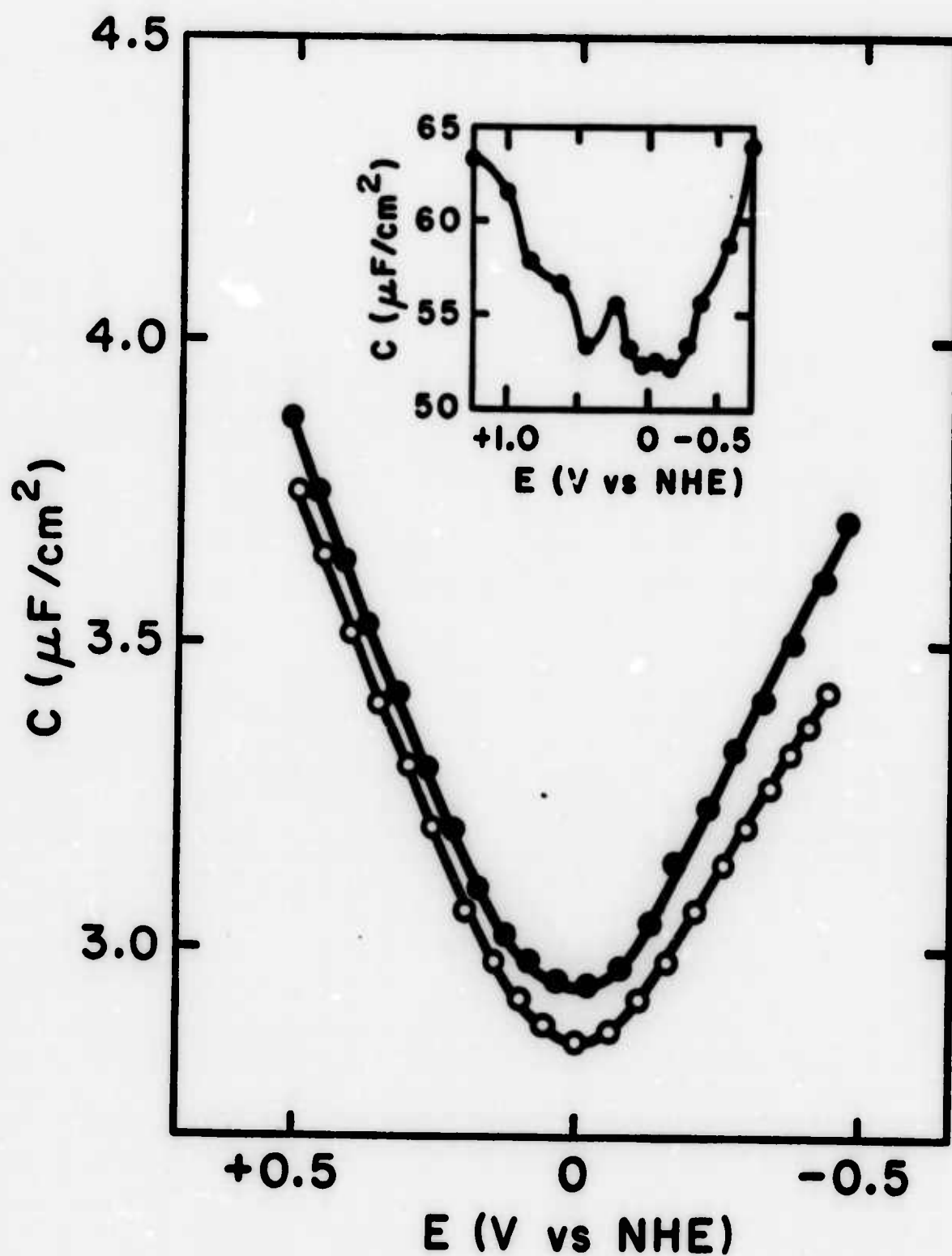


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